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CHEMFET CHEMICAL WARFARE AGENT DETECTOR

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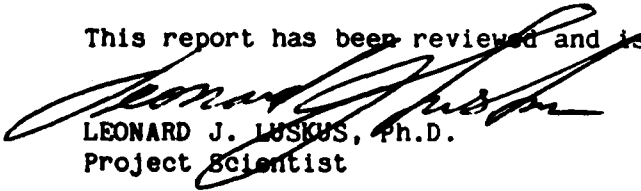
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In detector technology, one item whose feasibility as a cockpit chemical warfare agent detector has been demonstrated is the chemically sensitive field-effect transistor (CHEMFET). The overall objective of the present effort was: to test and evaluate CHEMFET semiconducting polymer gate electrode material; and to design, build, and optimize a breadboard detector by using selected material. A membrane consisting of a poly (vinyl pyrrolidone), poly (vinyl alcohol), and copper (II) bipyridine mix (the selected material) was cast over copper/copper (bipyridyl) electrodes to form a cell, the resistance of which was shown to change on exposure to organophosphonates and other vapors. These resistance changes, however, originated at the metal-polymer contact and were not due to change in bulk resistivity. Since this membrane could not then be used as a gas-sensitive layer in a CHEMFET structure (as had originally been hoped), the direction of the research was changed. Because of the extreme sensitivity of impedance measurements, made as a function of diisopropyl methylphosphonate (DIMP) and other organophosphorous vapor concentrations, an effort

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has been planned and is progressing towards building a dedicated battery-operated low-frequency bridge to measure the impedance of the organophosphonate sensitive resistance cell. Feasibility of this non-CHEMFET detector approach is being determined, with results to be presented in a subsequent technical report.

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CONTENTS

Illustrations

Figure
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1

CHEMFET CHEMICAL WARFARE AGENT DETECTOR

INTRODUCTION

The main objective of this work was to determine the origin of the change of resistance of the cell:metal/conducting polymer system/metal, with the change of partial pressure of certain organophosphates, and to construct a measuring system which could be used to detect these compounds. This work was the continuation of the study of conductivities of various polymers [1] as reported previously [2]. We hoped that the observed resistance changes were associated with the change of the bulk conductivity, in which case such materials could be used in solid-state detectors based on change of work function of this material on exposure to organophosphates [3].

EXPERIMENTAL MATERIALS AND METHODS

Chemicals

Used to form the polymeric membrane were: 2,2-bipyridine (Aldrich); copper (II) chloride (J. T. Baker); poly(vinyl pyrrolidone) (Polysciences); and poly(vinyl alcohol) (M.W. 86,000). The solvents used for casting were chloroform and carbon tetrachloride.

Diisopropyl methylphosphonate (DIMP) was obtained from Dr. E. S. Poziomek (Chemical Systems Laboratory, U.S. Army Armament Research and Development Command, Aberdeen Proving Ground, Md.). Dimethyl methylphosphonate (DMMP) (Aldrich) was also used as a model compound.

Apparatus

A Keithley 616 Electrometer was modified for alternating current impedance measurements as described in the "RESULTS AND DISCUSSION." An EXACT Model 126C sweep-frequency generator was used with a Houston 2000 X-Y recorder to record frequency dependence of impedance. The test chamber used for static response measurements had been described previously [2].

Throughout this report we have used, as the unit of concentration, parts per million--defined as X μl of pure compound injected into a volume of 1000 ml. Therefore, 1-ppm DMMP corresponds to 1 μl of pure DMMP introduced into a 1000-ml Erlenmeyer flask. All measurements were made at 25°C.

NOTE: The Chemical Systems Laboratory is now the Chemical Research and Development Center (CRDC).

RESULTS AND DISCUSSION

The polymer membrane originally proposed for this study [1] used poly(vinyl pyrrolidone) as the matrix. In the initial stages of this work we found that this membrane, which contains a small amount of water, dries up--particularly when the membrane is continuously exposed to low humidity air. This dryness leads to embrittlement and development of cracks which uncontrollably alter the overall electrical properties of this material. To circumvent this problem, we have modified the matrix by adding 50% poly(vinyl alcohol). Thus, the final composition of the membrane used in all subsequent studies was 39% poly(vinyl pyrrolidone), 39% poly(vinyl alcohol), 22% Cu(II) (bipyridyl) complex. Note that the Cu(II) (bipyridyl) was only partially dissolved in the polymer matrix; a large amount of solid crystalline material was always present in the membrane as the casting solvent ($CHCl_3/CCl_4$) evaporated. The final product was, therefore, a heterogeneous polymer material. This heterogeneity could be partially responsible for large variations in the baseline impedance, as will be discussed further.

Contact Versus Bulk Resistance

The fundamental question here is related to the origin of the measured resistance and to its changes with exposure to various organophosphates and other vapors. Our earlier experiments indicated that the organophosphate-related changes of resistance might be due to the change of contact resistance rather than to the change of the bulk conductivity of the active polymer. To distinguish between these two modes of response, we have prepared a substrate with regularly spaced contacts and measured the total resistance, R_{cell}, as a function of the contact distance. Two physical parameters contribute to the overall resistance: the resistance of the contact, R_c, and the resistance of the bulk membrane, R_b. For contacts of equal area:

$$R_{cell} = 2 R_c + R_b$$

However, because

$$R = \rho \frac{d}{A}$$

in which ρ is bulk resistivity of the material in ohms · centimeters, d is the distance between the contacts, and A is the cross-section of the membrane (or contact area):

$$R_{cell} = 2 R_c + (\rho/A) \cdot d$$

Therefore, the plot of R_{cell} vs. d (contact spacing) provides the necessary information about the origin of the resistance. Furthermore, the change of R_{cell} with the addition of the test compound is reflected in the change of the intercept (R_c) or of the bulk resistivity (ρ), and can be distinguished in these plots.

4

To test this hypothesis, we prepared regularly spaced contacts on a $Si/SiO_2/Si_3N_4$ substrate. The contact area was 1×10^{-4} cm^2 per contact. We expected that the contact material would affect R_c. Therefore, the following contacts were tested: platinum (Pt), gold (Au), and copper (Cu). The copper contacts were made by electroplating copper onto gold. The substrate was mounted on a ceramic header; each contact was wirebonded; and the whole assembly was then encapsulated in nonconducting EPON 826/Jeffamine D230 epoxy. The PVA, PVP, Cu(II) complex membrane was cast from $CHCl_3$ solution. No attempt was made to control the thickness of this membrane. All measurements were repeated with the Keithley 616 electrometer with the sample cell placed in a 500-ml Erlenmeyer flask, as described previously [1]. All measurements were made at room temperature.

Shown in Figure 1 is the dependence of direct-current resistance on the contact separation, d, for the gold/film/gold cell, in air and in 10 ppm DIMP. Relatively large scatter in the points is due to the fact that even a minute
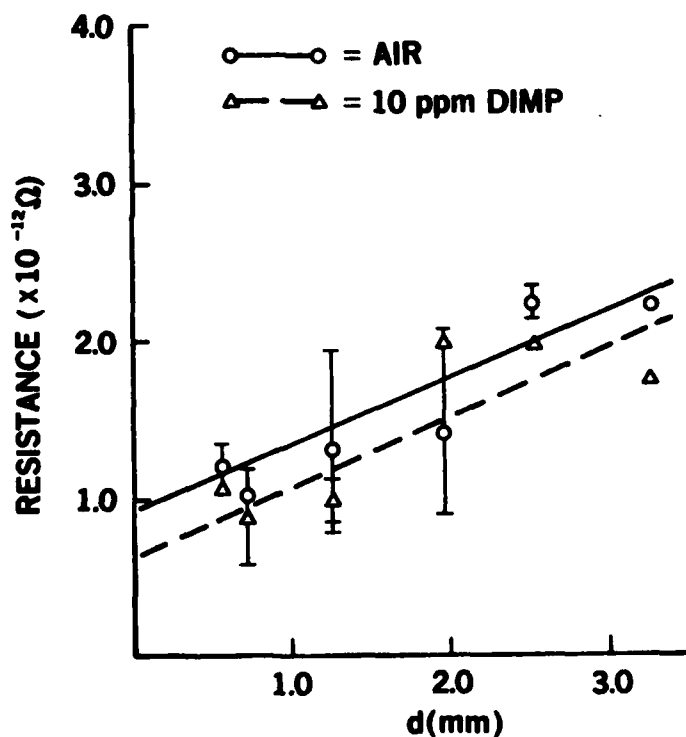

Figure 1. Dependence of the cell resistance, R_{cell}, on contact spacing, d, for air and for 10 ppm DIMP in air: Gold contacts.

5

amount of contaminants at the contact has a large effect on the contact resistance. Even though the cleaning cycle was the same for all samples tested, it is a parameter difficult to control. Despite this problem, the results in Figure 1 clearly indicate a substantial contact resistance ($R_c = 4.6 \times 10^{11}$) and $\rho = 3.8 \times 10^8$ Ωcm for the film in air.

The plot of R_{cell}, on distance d in the presence of DIMP, is parallel to but displaced by $1.5 \times 10^{11}\Omega$ at the intercept. Thus the lower value of $R_c = 3.1 \times 10^{11}$ is indicated, while ρ remains unchanged.

To investigate the effect of the contact material on R_c, we prepared a cell identical to the one used with Pt contacts (Pt/film/Pt). The results of the measurements are shown in Figure 2.
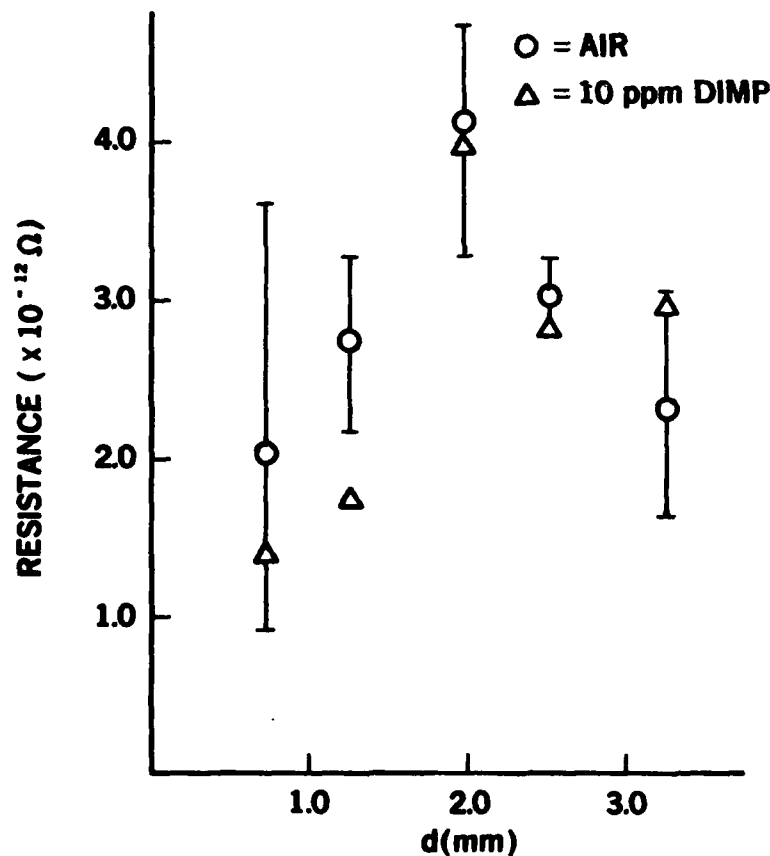

Figure 2. Dependence of the cell resistance, R_{cell}, on contact spacing, d, for air and for 10 ppm DIMP in air: Platinum contacts.

Response of the cell with equal size copper contacts (Cu/film/Cu) is shown in Figure 3. Also, a significantly lower resistance was obtained with the contacts treated with Cu(I) bipyridyl (Fig. 4). The procedure for contact treatment is given in the following section.

From these measurements we concluded that the observed direct-current resistance of the cell, metal/film/metal, was due mainly to the contact resistance which changed upon exposure to DIMP. In that case, the detection of organophosphates could not be done by measuring work-function difference between the polymer and the semiconductor, as originally proposed [2].
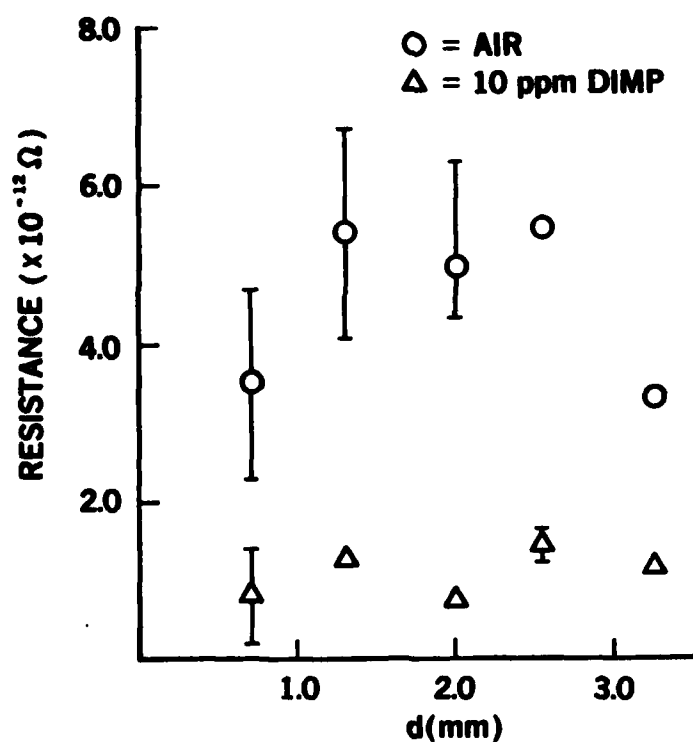

Figure 3. Dependence of the cell resistance, R_{cell}, on contact spacing, d, for air and for 10 ppm DIMP in air: Copper contacts.
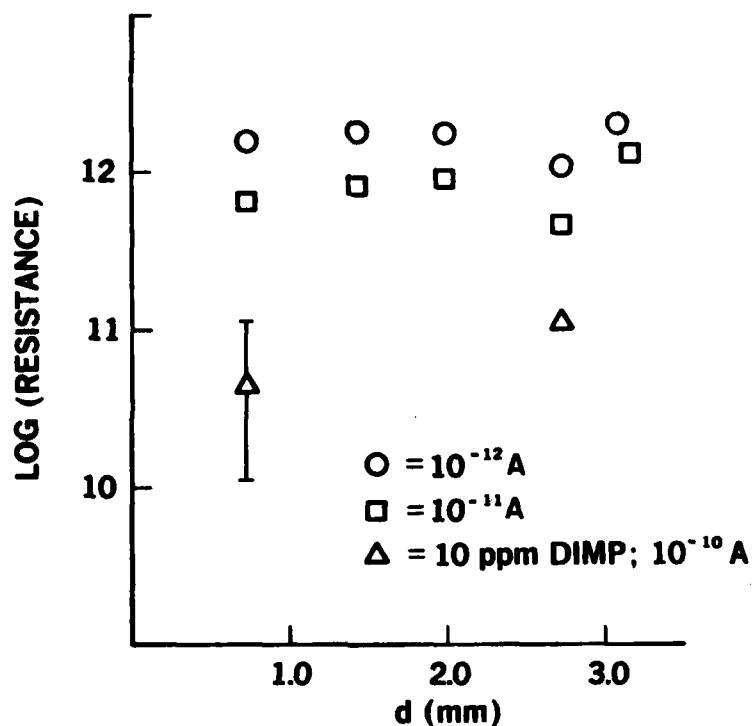
7

Figure 4. Dependence of the cell resistance, R_{cell}, on contact spacing, d, for air and for 10 ppm DIMP in air: Copper contacts treated with Cu(I)bipyridyl.

Impedance Measurements

We decided to investigate this mode of measurement because of the relatively high sensitivity of the resistance cell to organophosphates. Permission was requested, and granted, to engage Professor Dieter Gehmlich (Department of Electrical Engineering, University of Utah) in the project--with the specific task of designing the most suitable mode of impedance measurement. The direct-current mode of measurement may not be optimal; for the electrochemical changes which are taking place (namely, at the contacts) may lead to long-term polarization. Therefore, some mode of

8

cyclic measurement was thought to be preferable to the direct-current measurement. Secondly, since confining the geometry of the measuring cell to the geometry of CHFMFET chips was no longer necessary, cells with large contact areas also were studied.

Alternating Current Measurements

A new test system has been implemented so that alternating current measurements can be made on the chemical warfare (CW) agent detectors.

The Keithley electrometer was modified to accept an alternating current driving signal through an isolation transformer (Fig. 5).
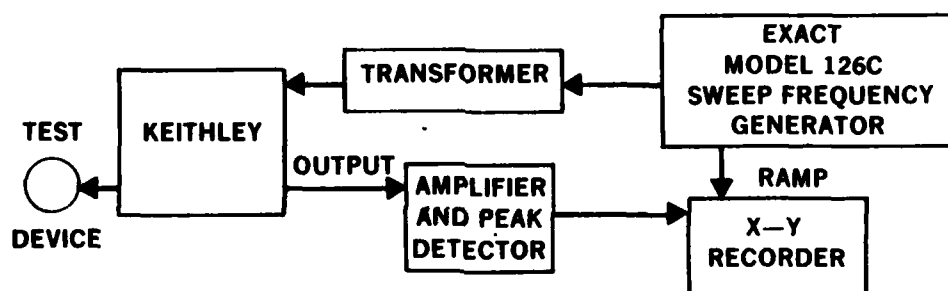

Figure 5. Alternating current measurement through an isolation transformer.

The EXACT Model 216C sweep generator was programmed to drive the Keithley through frequencies from 60 Hz to 21 kHz in two ranges. The output of the Keithley, amplified and peak-detected to provide a signal proportional to impedance, was recorded on the X-Y recorder as a function of frequency.

Test Devices

We have obtained several samples of Kapton ribbon (polyimide) with copper leads deposited on it. The membrane was cast on this tape. To obtain a better definition of the contact shown in area, three types of new test devices have been devised. They are of the format shown in Figure 6.
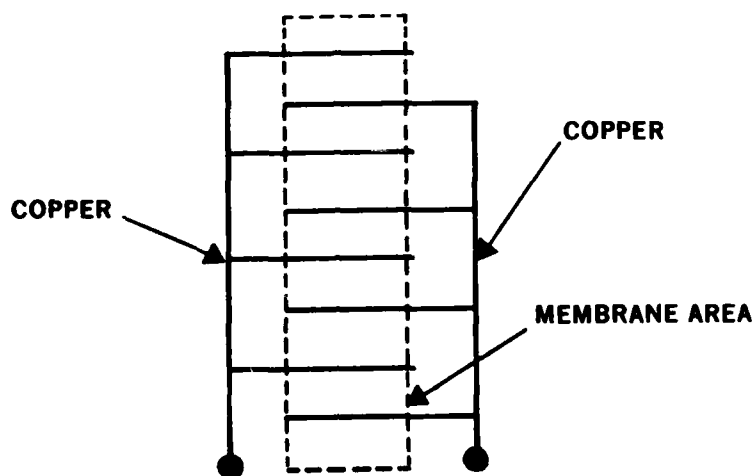

Figure 6. Configuration of the, test cell with large contacts.

Interleaved contacts of copper, covered by the sensitive membrane, provide multiple parallel paths through the membrane. As more parallel paths are used, the sensitivity should improve. The first device tested (device 1) has 8 copper contacts, providing 7 parallel paths. The copper elements were deposited on a flexible polyimide plastic base. Devices 2 and 3 have 20 and 60 copper contacts, respectively, and were made from printed circuit (PC) board materials by using standard PC board etching techniques.

In all the devices, the copper contacts were modified by the formation of Cu^{+1} bipyridyl on the copper surface. This layer was formed by completely cleaning the copper surface and then treating it with a solution of $CuCl_2$:

$$Cu^0 + Cu^{+2} = Cu^{+1}$$
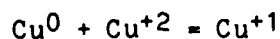
Next, the surface was rinsed with water and acetone and dried. The device was then dipped in a solution of 2,2'-bipyridine in toluene, which turned the surface black (or dark gray) immediately.

The membrane was cast from the mixture:

    0.28 g Cu(II) bipyridine
    0.5 g polyvinyl alcohol (86,000 MW)
    0.5 g polyvinyl pyrrolidone (PVP)

in a 50/50 $CHCl_3/CCl_4$ solvent system.

Tests run on device 1 have indicated improved sensitivity, particularly at low frequencies (near 60 Hz). Shown in Figure 7 is an X-Y recording of
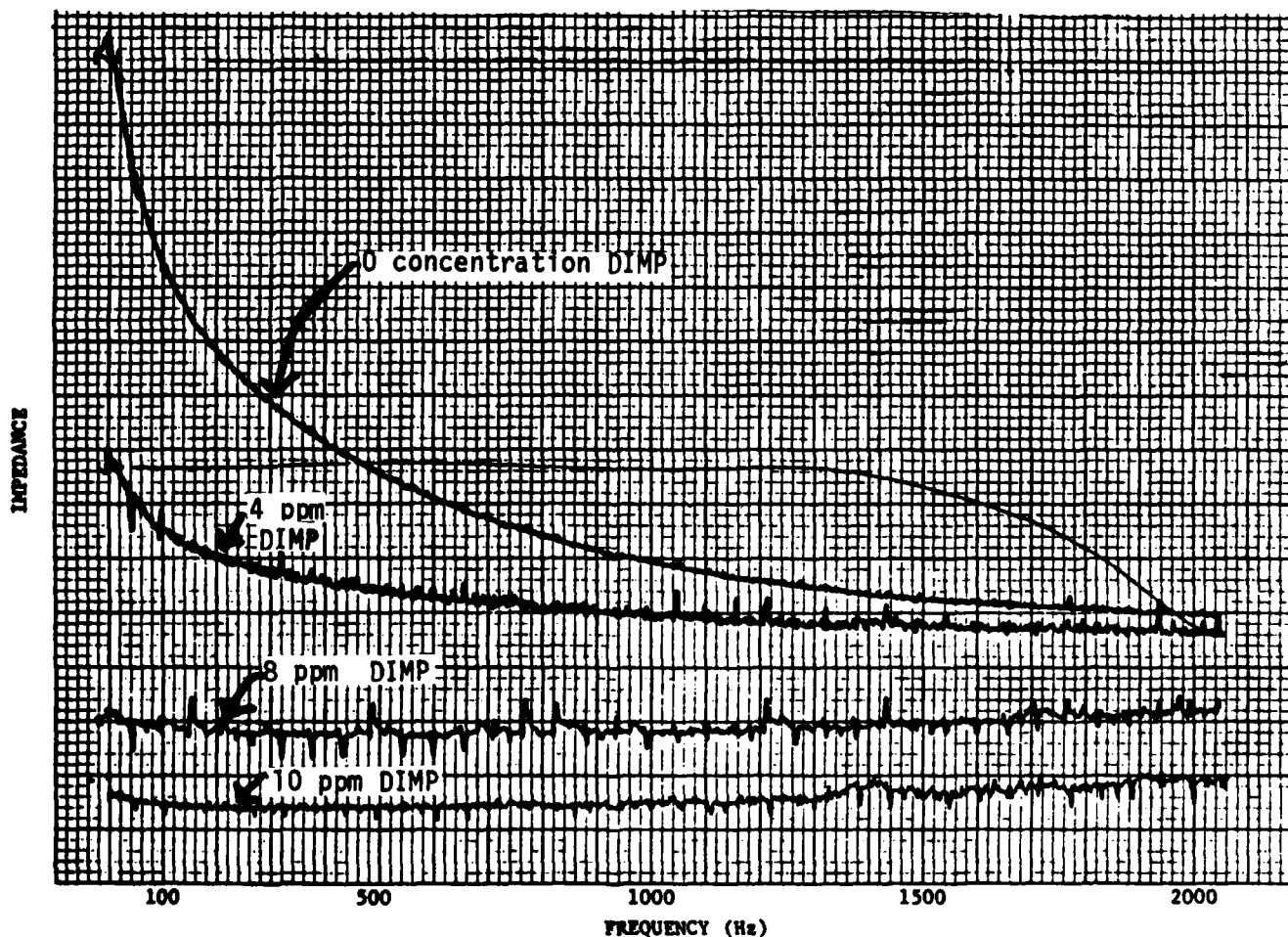

Figure 7. Frequency dependence of the cell impedance for different concentrations of DIMP: Range 60 to 2000 Hz.

11

device impedance for 0, 4, 8, and 10 ppm DIMP over the frequency range 60 to 2000 Hz. Decreased separation at higher frequencies is shown in Figure 8.
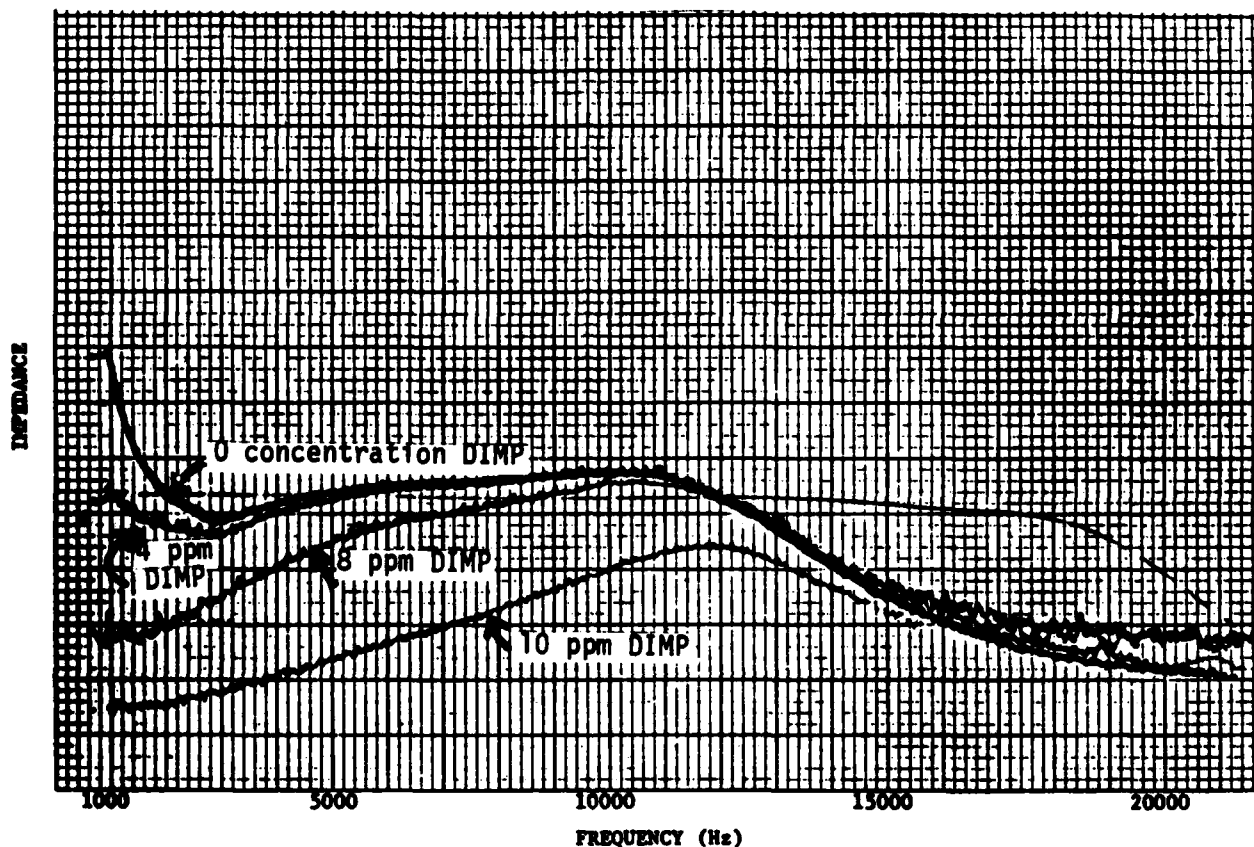

Figure 8.   Frequency dependence of the cell impedance for different concentrations of DIMP (same as Fig. 7): Range 1 to 21 kHz.

A number of tests have been run to determine if the apparent "peaking" at 12 kHz has significance. We found that capacitances in the Keithley and the leads account for the apparent impedance changes in the high-frequency range. At this time, we feel that the most useful data will be obtained at low frequencies.

Different Electrode Configurations

To determine the detection limit, the effect of contact area has been investigated by connecting 10 or 30 contacts in parallel. All of these measurements were repeated in the direct-current mode, because our previous results have clearly shown that the sensitivity decreases with increasing

12

frequency. The detection limit obtained with the 30-contact device was 1-ppm DMMP, with a time response of approximately 25 sec. The detection limit of a 10-contact device was approximately 3 ppm with the same time response. The resistance measurements in the direct-current mode are, however, subject to very large errors due, namely, to the long-term instability of the baseline.

CONCLUSIONS

The work performed in this portion of the contract can be summarized as follows:

1. The modified membrane cast over copper/Cu(bipyridyl) contacts forms a cell, resistance of which changes upon exposure to organophosphates and other vapors.

2. These resistance changes originate at the metal-polymer contacts, and are not due to the changes of bulk resistivity.

3. This membrane material cannot be used as a gas-sensitive layer in a CHEMFET structure, as had been originally hoped.

4. The sensitivity of the impedance measurement to changes in partial pressure of DIMP or DMMP decrease with increasing frequency.

5. The direct-current mode of measurement, although most sensitive, is also most unstable.

6. The devices are very sensitive to water vapor.

7. The detection limit for DMMP is 1 ppm with a time constant of 25 sec.

RECOMMENDATIONS

We recommend building a dedicated battery-operated low-frequency impedance bridge to measure the impedance of the organophosphate sensitive resistance cell. To eliminate the interferences from other vapors (e.g., water, alcohols, and cigarette smoke), we further recommend that an identical cell be placed in the opposing arm of the impedance bridge. This cell should incorporate a membrane material which is sensitive to water vapor and possibly to other interferents, but insensitive to the compounds of interest. A possible candidate for such material could come from the group of membranes which were reported to have low or no response to organophosphates [1]. The material investigated during this period of the contract is not suitable for a direct CHEMFET application. However, the principles of CHEMFET-sensing organophosphates [2] still hold. A suitable material must be found which will have desirable electrical and chemical properties for that purpose.

13

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